

Stable and Radio Isotope Analysis to Identify Sources of Methane during a Remedial Action

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Background/Objectives. Methanogens/Archaea are often the dominant microbes in reduced environments and methanogenesis is a requisite component of anaerobic bioremediation. If Archaea are not controlled, then in situ remedial actions employing conventional (i.e., no active control of Archaea) amendments such as [emulsified] oils/lecithins, lactates/sugars, simple hydrogen release compounds, EHC®) can generate excessive amounts of methane. However, methane in ecosystems can also originate thermogenically from regions of petroleum formation deep within the earth and/or via microbial fermentation of indigenous organic carbon and subsequent microbial reduction of carbon dioxide. Hence, the origin of methane is not always clear.

Approach/Activities. Such was the situation where Provect-IR® antimethanogenic ISCR reagent was applied to treat chlorinated solvents in groundwater at a former dry cleaner facility. The technology rapidly and effectively reduced the concentration of PCE in groundwater thus meeting the project goals without the accumulation of catabolites (TCE, DCE or VC) and without excessive methanogenesis (e.g., <2 mg/L) in the treated area. However, about 9 months post-treatment, methane (5 to <10 mg/L) was observed downgradient of the treated areas. The source of the methane was potentially a result of the remedial action because: i) the area with elevated CH₄ did not have methane control technology, and ii) the response was coincidental with amendment application. Alternatively, the methane was not a direct result of the remedial action, noting: i) the area of interest was directly associated with gasoline/Diesel USTs (removed but no active remediation was performed), ii) the soil gas contained CH₄ along with BTEX and other gasoline COIs, iii) methane is generated (in large quantities) during the biodegradation of gasoline under hypoxic conditions, and iv) there was <500 ppm TOC in groundwater emanating from the upgradient Provect-IR treatment area (unlikely to produce that much CH₄). In addition, there were sewer lines, utilities, multiple gasoline stations, and operation industrial activities in the immediate area.

Results/Lessons Learned. Carbon isotope analyses - radiocarbon (¹⁴C) and stable carbon (¹³C) – were coupled with methane (CH₄) and carbon dioxide (CO₂) data from groundwater samples to determine the origin of the respired carbon. This combination of both gasses provides an estimate of total degradation by assuming microbial degradation to CO₂ and, when there is active degradation, CO₂ is further reduced to CH₄. The ¹³C range for carbon sources respired in the process would be approximately -26.5‰ and 33.0‰ for Provect-IR and TPH residuals, respectively. ¹⁴C is approximately 0‰ and -999‰ for Provect-IR (young carbon) and TPH (old carbon), respectively. The large data range for ¹⁴C provides strong capability to confirm degradation. Data from these analyses can support a fourth scenario where methane was an “indirect” response to treatment where dissolved constituents of the ISCR amendment migrated down-gradient and stimulated the biodegradation of TPH residuals. This scenario would be relevant to other urban settings where dry cleaning operations were located on former gasoline/UST sites.